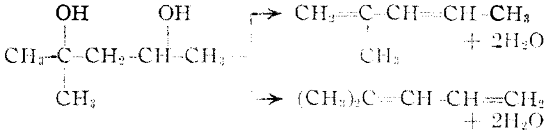
[A CONTRIBUTION FROM THE LABORATORIES OF THE SHELL DEVELOPMENT COMPANY]

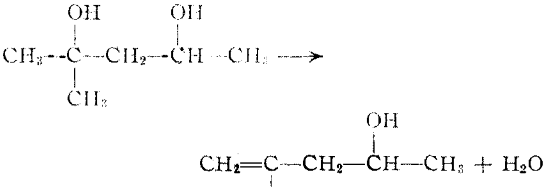
3,6-Dihydro-2,4,6-trimethyl-2H-pyran, a Product of the Dehydration of 2-Methyl-2,4-pentanediol

BY SEAVER A. BALLARD, ROY T. HOLM AND PAUL H. WILLIAMS

The dehydration of 2-methyl-2,4-pentanediol was reported by Kyriakides[1] to yield 4-methyl-1,3-pentadiene and an unsaturated alcohol distilling in the neighborhood of 130° to which was assigned the structure of 4-methyl-3-penten-2-ol. The work of subsequent investigators revealed that the hydrocarbon product is a mixture of 2-methyl-1,3-pentadiene and 4-methyl-1,3-pentadiene, with the former predominating,[2] and that the true structure of the alcohol is that of 4-methyl-4-penten-2-ol.[3] The reactions by which these products are formed may be represented as

(1)


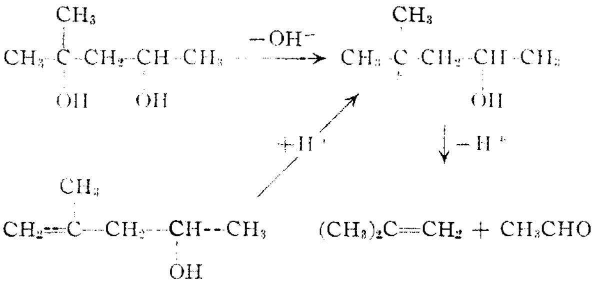
$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{OH}{CH}-CH_3 \begin{cases} \rightarrow CH_2{=}\underset{CH_3}{C}-CH{=}CH-CH_3 + 2H_2O \\ \rightarrow (CH_3)_2C{=}CH-CH{=}CH_2 + 2H_2O \end{cases}$$

(2)


$$CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_2-\overset{OH}{CH}-CH_3 \longrightarrow CH_2{=}\underset{CH_3}{C}-CH_2-\overset{OH}{CH}-CH_3 + H_2O$$

In addition to the methylpentadienes, Ipatieff and Pines[4] have reported the formation of 1,3,4-trimethyl-5-isopropenyl-1-cyclohexene (a diene dimer) and small amounts of 1,3,5-trimethylcyclohexene, unidentified aromatic hydrocarbons, and an unsaturated ether of undetermined structure distilling at about 135–140° on heating either 2-methyl-2,4-pentanediol or 4-methyl-4-penten-2-ol under pressure with a dilute aqueous solution of ferric chloride and magnesium chloride. Dehydration of the diol by means of iodine gave, in addition to the unsaturated alcohol, a 2% yield of a material boiling at 139–141° which appeared to be 2,2,4,4,6-pentamethyl-*m*-dioxane.

In the course of preparing large quantities of the methylpentadienes in this Laboratory, an opportunity was afforded to study fully the dehydration of 2-methyl-2,4-pentanediol. In so doing, the more recently assigned structures of the methylpentadienes and the methylpentenol were confirmed and, also, acetaldehyde and isobutylene were isolated and identified as by-products of the reaction. The latter two substances were recoverable in yields of approximately 2% and 4%, respectively, from iodine-catalyzed dehydrations and presumably resulted from a beta-fission of the diol, 4-methyl-4-penten-2-ol or of both[5]; the fissions may be postulated as proceeding through a common carbonium ion intermediate[6]



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{-OH^-} CH_3-\overset{CH_3}{\underset{+}{C}}-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{-H^+} (CH_3)_2C{=}CH_2 + CH_3CHO$$

$$CH_2{=}\overset{CH_3}{C}-CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{+H^+} CH_3-\overset{CH_3}{\underset{+}{C}}-CH_2-\underset{OH}{CH}-CH_3$$

The unsaturated alcohol fraction of the product formed in the present work contained considerable amounts of a non-alcoholic component, as has been noted also by Ipatieff and Pines. This component, distilling over the range of 132–140° (mainly 132–137°) *when free of alcohol*, was identified in the study here reported as 3,6-dihydro-2,4,6-trimethyl-2H-pyran (I) along with a small amount, perhaps 10%, of an isomeric substance indicated to be 2,6-dimethyl-4-methylenetetrahydropyran (II)[7]; this mixture was formed in yields of as high as about 7% in the dehydration of the diol. 3,6-Dihydro-2,4,6-trimethyl-2H-pyran (I) boils at 136.4° and was obtained nearly free of the isomeric pyran, 2,6-dimethyl-4-methylenetetrahydropyran (II), by careful fractional distillation. The latter substance appeared in the fractions distilling between 132.0 and 136.4° but could not be obtained in high purity by distillation.

Minor constituents of the non-alcoholic component (occurring principally in the boiling range 137–140°) were not identified but may have included the cyclic acetal of the diol, 2,4,4,6-tetramethyl-*m*-dioxane, and/or the product isolated by Ipatieff and Pines[4] and tentatively identified by them as 2,2,4,4,6-pentamethyl-*m*-dioxane.

Identification of the Pyran Mixture

The composition of the non-alcoholic component was established as a mixture of the pyrans I and

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[1] Kyriakides, THIS JOURNAL, **36**, 994 (1914).

[2] Farmer, *et al.*, *J. Chem. Soc.*, 511 (1930); 3221 (1931); 1065 (1937); Bachman and Goebel, THIS JOURNAL, **64**, 787 (1942).

[3] Kenyon and Young, *J. Chem. Soc.*, 1452 (1938); du Pont and Darmon, *Soc. chim. de France*, [5] **6**, 1208 (1939).

[4] Ipatieff and Pines, THIS JOURNAL, **67**, 1200 (1945).

[5] Schmerling, Friedman and Ipatieff, *ibid.*, **62**, 2446 (1940), and Finch and Ballard (to Shell Development Co.), U. S. 2,421,554 (June 3, 1947) have reported that acetaldehyde and isobutylene are the *chief* products of the vapor phase dehydration of the diol.

[6] According to the theory advanced by Whitmore, Krimmel and Cook, American Chemical Society, Division of Organic Chemistry, New York, September, 1944, Abstracts, page 21M; Whitmore, *Chem. Eng. News*, **26** [10], 671 (1948).

[7] Schelling and Anderson (to Shell Development Co.), U. S. 2,422,802 (June 24, 1947); Williams and Ballard (to Shell Development Co.), U. S. 2,452,977 (Nov. 2, 1948).

II by its chemical properties, by degradation reactions, by its conversion to 2,4,6-trimethyltetrahydropyran-4-ol (III) and by comparison of its physical properties and infrared absorption spectrum with those of an independently synthesized sample of a mixture of I and II.

The mixture in question has an elemental composition corresponding to the empirical formula $C_8H_{14}O$. It absorbed one mole of bromine per formula weight and reacted but negligibly with analytical reagents for carbonyl and hydroxyl groups. It was concluded from this evidence that the material was essentially an unsaturated cyclic ether.

Hydrogenation of the cyclic ether resulted in the absorption of one equivalent weight of hydrogen to form the substance now known as the tetrahydropyran, IV. Cleavage of IV with acetyl chloride led through the steps indicated to 4-methylheptan-2-ol (VII), which in turn was identified by its conversion to the 4-methylheptenes (IX) and, finally, to 4-methylheptane (X). The exact location of the chlorine atom in product V was not indicated by these reactions and hence the identity of only one of the oxygen-bridged carbon atoms in the original cyclic ether was established by this degradation.

The action of 66% sulfuric acid on the unsaturated cyclic ether yielded 2,4,6-trimethyltetrahydropyran-4-ol (III). This alcohol had a distilling range of 84 to 89° at 18 mm. (183 to 189° at 762 mm.) and melting point of about 30°. It was separated into two distinct fractions by distillation and crystallization, the lower boiling one melting at 41° and the higher one at 51.5°; these were identical with corresponding fractions of 2,4,6-trimethyltetrahydropyran-4-ol synthesized by reaction of the methyl Grignard reagent with 2,6-dimethyltetrahydro-1,4-pyrone.[8] The two forms of 2,4,6-trimethyltetrahydropyran-4-ol have not been reported previously; they are undoubtedly simply two of the three geometrical forms (related to one racemic and two *meso* modifications) in which this substance might exist.[9]

The formation of 2,4,6-trimethyltetrahydropyran-4-ol by hydration shows the basic pyran structure of the cyclic ether mixture and indicates that the unsaturated linkages in the principal components of the latter material are situated about the carbon atom in position four of the ring. The infrared absorption spectrum of the pyran mixture has strong bands which indicate the presence of unsaturation in *both* of the two possible positions about this carbon atom.[10] Further, the only slight reactivity of the mixture with hydroxylamine hydrochloride solution (accountable for by the presence of a trace of mesityl oxide) and its non-reactivity with water[11] as well as its infrared absorption spectrum, indicates the absence of isomers with unsaturation about position 2. These facts are believed to constitute adequate evidence of the presence of both 3,6-dihydro-2,4,6-trimethyl-2H-pyran (I) and 2,6-dimethyl-4-methylenetetrahydropyran (II) in the mixture and the absence, except perhaps in very minor amounts, of other isomeric pyrans.

Mechanisms for the formation of 3,6-dihydro-2,4,6-trimethyl-2H-pyran (I) and 2,6-dimethyl-4-methylenetetrahydropyran (II) during the dehydration of 2-methyl-2,4-pentanediol are suggested and experimentally demonstrated in the following paper.

The authors thank Drs. R. R. Brattain and the late R. S. Rasmussen of Shell Development Company for determining and interpreting the infrared absorption spectra discussed in this paper. They also wish to acknowledge the work of Mr. H. de V. Finch, who first recognized that the diol dehydration product contained the material which the authors later isolated in pure form and identified as the pyran mixture.

Experimental[12]

Source and Isolation of the Pyran Mixture.—The conditions and catalyst employed for the dehydration of 2-methyl-2,4-pentanediol depended upon whether the purpose was production in maximum yield of 4-methyl-4-penten-2-ol or of methylpentadiene. The dehydrations were carried out in a glass vessel under a fractionating column equipped with a total-condensation, partial-take-off, phase-separating head. In many instances, in order to process large quantities of diol, an initial charge of diol was made to the reactor and further diol was then charged continuously during the dehydration at approximately the rate of its consumption.

For maximum yield of the methylpentenol the still was set at total-take-off to remove products of dehydration from

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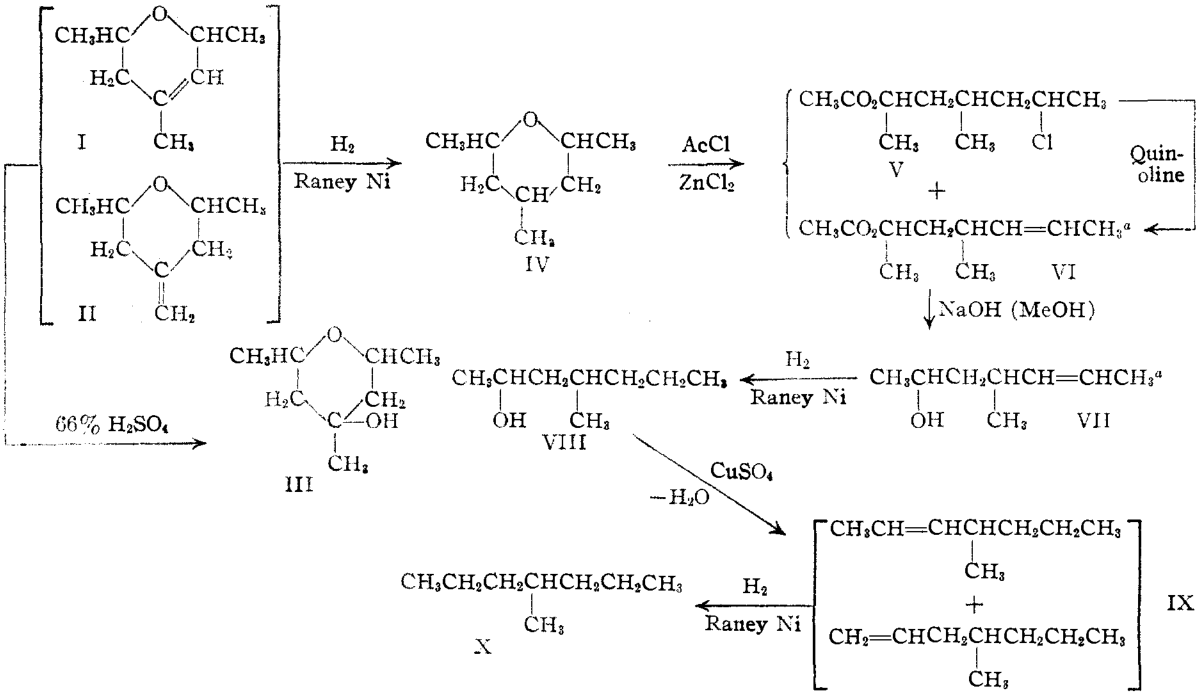
(8) Borsche and Thiele, *Ber.*, **56B**, 2012 (1923).

(9) de Vrieze, *Rec. trav. chim.*, **66**, 486 (1947) (see also Cornubert and Viroit, *Compt. rend.*, **224**, 1114 (1947)), regarded 2,6-dimethyltetrahydropyran-4-ol, obtained by hydrogenation of 2,6-dimethyl-1,4-pyrone over Raney nickel activated with platinum chloride, as a mixture of two geometrical isomers which differ only in respect to the position of the hydroxyl group and the hydrogen atom bonded to the carbon of position 4, the two methyl groups in each isomer occupying the *cis* position. If it is assumed that the *cis* isomer of 2,6-dimethyltetrahydro-1,4-pyrone is formed on *partial* hydrogenation of 2,6-dimethyl-1,4-pyrone (regardless of the catalyst employed), and that these methyl groups remain *cis* on converting the compound to 2,4,6-trimethyltetrahydropyran-4-ol, it may be concluded that the isomers of the latter substance obtained as in the present work represent the *cis-cis-cis* and *cis-cis-trans* configurations.

(10) The positions of the double bonds in the pyran mixture and in the olefin mixture IX were clearly indicated by their infrared absorption spectrum from 2 to 15μ. The strong bands in the region 10 to 13μ, which are characteristic of the type of substitution around carbon-carbon double bonds, indicate that the pyran mixture consists of substances containing unsaturated linkages of the types $R_2C{=}CH{-}R$ and $R_2C{=}CH_2$. The latter type was estimated to be present to the extent of about 10% in the mixture. There was inconclusive evidence of the presence of small amounts (less than 5%) of other isomeric pyrans in the mixture. Similarly, the olefinic hydrocarbon IX was indicated to be a mixture of $R{-}CH{=}CH{-}R$ and $R{-}CH{=}CH_2$ types of olefins with the former predominating; hydrocarbon IX was therefore a mixture of 4-methyl-1-heptene and -2-heptene. (R means a hydrocarbon radical or part of a ring system and not hydrogen.) These conclusions are based on data obtained with unsaturated hydrocarbons, as reported by Rasmussen, *et al.*, *J. Chem. Phys.*, **15** [3], 120, 135 (1947).

(11) Perkin, Jr., *J. Chem. Soc.*, 724 (1887).

(12) Melting points and boiling points are uncorrected. All distillations were carried out in vacuum-jacketed, helix-packed (unless otherwise specified) columns fitted with total condensation-partial take-off heads. Pressures below atmospheric were measured with U-type mercury-filled manometers.



[a] The isomer having the unsaturated linkage in the 6,7-position may also be present.

the reaction zone as rapidly as formed; copper sulfate was used as a catalyst (about 0.4 g. per mole in the initial charge). In a typical run the yield of diene was only 21.5% and the alcohol fraction of the distillate, b. p. 129–132°, containing 87% (by hydroxyl value) of alcohol, represented alcoholic and non-alcoholic component (as $C_8H_{14}O$) yields of 58.8 and 6.9%, respectively; 16% of the diol was recovered unchanged. Acetaldehyde and isobutylene were also formed during the dehydration and were isolated in yields of 1% or less; the former was identified by its 2,4-dinitrophenylhydrazone and the latter by Podbielniak distillation and by absorption in 65% sulfuric acid.

The non-alcoholic component and the methylpentenol form an azeotrope boiling at 129–130° and containing about 57% of the alcohol. Isolation of the non-alcoholic component from crude alcohol-rich fractions was accomplished either by treatment of the mixture with acetic anhydride followed by removal of the alcohol as the acetate (b. p. 150.1–150.2° at 763 mm.; n^{20}_D 1.4167; d^{20}_4 0.8857) or by dehydration of the alcohol to methylpentadiene which distils at 75–77°.

When dehydration of the diol was for maximum diene yield, iodine was used as catalyst (about 0.05 g. per mole in initial charge and in feed stock) and the take-off of organic product at the stillhead was regulated at such a rate as to maintain the stillhead temperature at 70° or below; the unsaturated alcohol was thus continuously returned to the reactor to effect its further dehydration. In a typical run conversion of diol was 99%, yield of diene was 84%, and the alcohol fraction content of the reaction distillate was negligible; the yields of acetaldehyde and isobutylene were estimated at about 2 and 4%, respectively. The reaction residue, in addition to diene dimer and higher polymers and condensates, contained a fraction distilling from 125 to 145° (mainly 130 to 140°) and containing a minor amount of methylpentenol; the non-alcoholic component of this fraction (yield about 4%) appeared from its properties to be substantially the same as the corresponding product resulting from the copper sulfate-catalyzed dehydration.

The combined bottoms from several iodine-catalyzed dehydrations carried out as described above served as the source of most of the non-alcoholic component used in this investigation; the crude fraction distilling over the range 125 to 145° was utilized. The alcohol remaining in this fraction was removed by treatment of the mixture with 0.5% of concentrated sulfuric acid under a column at reflux temperature distilling off methylpentadiene and water as formed. When no further dehydration occurred, the content of the reaction flask was washed with aqueous sodium hydroxide, dried and then carefully fractionated through a 140 × 1.2 cm. column; the material distilled chiefly over the range 132 to 140° (760 mm.) in the following composited fractions: Fraction (a): 15.5%, b. p. 132.0–136.2°, n^{20}_D 1.4400–1.4402. Fraction (b): 62%, b. p. 136.2–136.6°, n^{20}_D 1.4402–1.4403. Fraction (c): 22.5%, b. p. 136.6–140.0°, n^{20}_D 1.4402–1.4379. A fraction of b. p. 136.4°, n^{20}_D 1.4403, d^{20}_4 0.8629 appeared to represent a single component of the original mixture.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.10; H, 11.18.

A sample of the full boiling range material (132–140°), n^{20}_D 1.4400, d^{20}_4 0.8652, had the following elemental composition: C, 75.74; H, 11.25. Reaction with bromide-bromate reagent gave a bromine number of 128 g. Br_2 per 100 g. (theoretical bromine number for one unsaturated linkage, 126.6 g.). It was not cleaved by water at 200° for eight hours and reacted with but 0.05 equivalent of hydroxylamine hydrochloride per 100 g. of pyran when treated with an aqueous ethanolic solution of this reagent at 60° for two hours.[13] The presence of but 0.003 equivalent of hydroxyl per 100 g. of pyran was determined by treatment with acetyl chloride-pyridine reagent.[14]

The pyran mixture has a characteristic ether-like odor.

Infrared Absorption Spectra.—Various fractions of the pyran mixture were examined spectroscopically. The components of the full range material (b. p. 132–140°) were found to represent two types of carbon–carbon unsaturation.[10] These components were subsequently identified as the pyrans I and II. The fraction with b. p. 136.4° appeared from its spectrum to be substantially pure I. Higher boiling fractions were largely I with traces of unidentified impurities; lower boiling fractions contained both I and II, as well as a carbonylic impurity (less than 1%) which was identified as mesityl oxide (2,4-dinitrophenylhydrazone, m. p. 206°, mixed m. p. 206°).

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(13) Bryant and Smith, THIS JOURNAL, 57, 57 (1935).

(14) Smith and Bryant, *ibid.*, 57, 61 (1935).

Hydrogenation of the Pyran Mixture.—A 716 g. (5.7 moles) quantity of the pyran mixture was shaken with 25 g. of Raney nickel and hydrogen at maximum temperature and pressure of 150° and 1500 p.s.i., respectively. Approximately a molar equivalent of hydrogen was absorbed. The product (IV) distilled at 129.4-136.4° (90% at 130-133°) and had n^{20}_D 1.4220 and d^{20}_4 0.8389. Reaction with bromide-bromate reagent indicated that it contained 1.5% unsaturated material. Reaction with acetyl chloride-pyridine reagent[14] showed the presence of less than 1% of alcoholic impurity. The material had a pleasant terpene-like odor.

Cleavage of IV with Acetyl Chloride[15] and Subsequent Reactions.—To a stirred mixture of 573 g. (4.5 moles) of IV, b. p. 129.4-136.4° (759 mm.), and 5 g. of zinc dust heated to and maintained at 90-95° was added dropwise 550 g. (7.0 moles) of acetyl chloride over a period of two hours. The dark colored product on cooling was diluted with an equal volume of water. The organic layer which separated was washed well with water, neutralized with aqueous sodium carbonate and distilled. In this way were obtained: 210 g. of unreacted pyran mixture; 112.5 g. (23% yield) of an octenyl acetate (VI), b. p. 49.8-51.6° (5 mm.), n^{20}_D 1.4270, d^{20}_4 0.8782; 442.5 g. (75% yield) of the acetate of a chlorooctanol (V), b. p. 65.5-66.0° (2.5 mm.), n^{20}_D 1.4371, d^{20}_4 0.9892.

Anal. Calcd. for $C_{10}H_{18}O_2$ (VI): sapn. equiv., 170.24; bromine number, 93.83 g. Br/100 g. Found: sapn. equiv., 171.8; Br no., 92.7 g. Br/100 g. Calcd. for $C_{10}H_{19}OCl_2$ (V): Cl, 17.15. Found: Cl, 17.3.

Saponification of the acetate (VI) yielded (95%) an alcohol (VII) of b. p. 68.6-69.0° (15 mm.), 3,5-dinitrobenzoate, m. p. 57.0-57.5°.

Anal. Calcd. for $C_{15}H_{18}O_6N_2$: C, 55.89; H, 5.63; N, 8.69. Found: C, 55.5; H, 5.8; N, 8.7.

On hydrogenation over Raney nickel at 100° and 800 p.s.i. VII was converted to an octanol (VIII), b. p. 169.6-170.0° (764 mm.), n^{20}_D 1.4252, d^{20}_4 0.8220.[16]

Anal. Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.93. Found: C, 73.60; H, 13.94.

The 3,5-dinitrobenzoate of VIII melts at 49.5-50.0°.

Anal. Calcd. for $C_{15}H_{20}O_6N_2$: C, 55.55; H, 6.22; N, 8.64. Found: C, 55.5; H, 6.3; N, 8.6.

Treatment of the acetate of the chlorooctanol (V) with 0.55 molar equiv. of quinoline in benzene solution at about 140° gave (65% yield) an ester of b. p. 50-55° (5 mm.). Saponification of this ester with methanolic sodium hydroxide resulted in an alcohol (90% yield), the 3,5-dinitrobenzoate of which was shown (by m. p. 57.0-57.5°, mixed m. p. 57.0-57.5°) to be identical with the same derivative from VIII.

Dehydration of the octanol (VIII) by refluxing in the presence of anhydrous copper sulfate yielded (70% conversion) an olefinic hydrocarbon mixture (IX),[10] b. p. 113.1-113.6° (762 mm.). Hydrogenation of IX in the presence of Raney nickel at 100° and 500 p.s.i. yielded a saturated hydrocarbon (X), b. p. 117.4-117.6° (762 mm.), n^{20}_D 1.3985, identified as 4-methylheptane.[17]

Hydration of the Pyran Mixture.—In a typical experiment, 126 g. (1.0 mole) of the pyran was treated at 10-20° with 225 ml. of 66% sulfuric acid. After standing an hour the reaction mixture was poured over an equal weight of ice and neutralized with aqueous sodium hydroxide. The organic layer which formed was separated and the aqueous layer was extracted with diethyl ether. Distillation of the combined organic layer and ether extract gave 20 g. of unreacted pyran mixture and 98 g. (81% yield) of the hydrate (III), b. p. 84-89° (18 mm.) (183-189° at 762 mm.), n^{20}_D 1.4510, d^{20}_4 0.9643. The hydrate (III) was miscible with water, hydrocarbons and other organic solvents. On cooling below 0° it solidified to a crystalline mass, m. p. *ca.* 30°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 66.64; H, 11.20.

Reaction of III with 100 mole % excess of acetic anhydride gave a 78% yield of an acetate, b. p. 86-88° (16 mm.).[18] This product had a saponification equivalent of 185 (calcd. for $C_8H_{15}O(OCOCH_3)$, 186.24).

Fractional distillation of a 500-ml. sample of III through a 20-bubble plate column yielded material of distilling range 182.2 to 189.8° (771 mm.) which was separated into a main fraction of b. p. 183.6-185°, n^{20}_D 1.4508-1.4509, and a minor fraction of b. p. 188.8-189.8°, n^{20}_D 1.4534. Both of these fractions crystallized on cooling and were then recrystallized from isopentane. The lower boiling fraction formed hygroscopic rhombohedral crystals, m. p. 41°, and the higher boiling one formed fine needles, m. p. 51.5°. A mixture of the two crystalline materials melted below 30°. Intermediate fractions from the distillation, some of which crystallized on seeding, contained substantial amounts of one or the other of these two crystalline materials. The mixture as a whole appeared to be chiefly the lower boiling, lower melting product.

The infrared absorption spectra of the two crystalline components of III were identical except for small differences in intensities of absorption at certain bands.

Synthesis of 2,4,6-Trimethyltetrahydropyran-4-ol.[8]—2,6-Dimethyl-1,4-pyrone was prepared by refluxing dehydracetic acid with concentrated hydrochloric acid according to the method of Collie,[19] but his procedure was modified so that after concentrating the hydrochloric acid solution of the product on the steam-bath, it was neutralized with aqueous sodium carbonate and evaporated to dryness. The solid product obtained was Soxhlet-extracted with isooctane. In this way crude 2,6-dimethyl-1,4-pyrone, m. p. 124-135°, was obtained in 85% yield. Recrystallization from absolute ethanol gave a product of m. p. 131-132° (picrate, coarse yellow needles (from water), m. p. 101.0-101.4°).

2,6-Dimethyltetrahydro-1,4-pyrone was prepared in 66% yield by hydrogenation of 2,6-dimethyl-1,4-pyrone over palladium chloride at room temperature and pressure of 6 to 16 p.s.i.g., according to a modification of the method of Borsche.[8,20] It had b. p. 170.5-171.5° (760 mm.), n^{20}_D 1.4435, d^{20}_4 0.9742, and formed a 2,4-dinitrophenylhydrazone, m. p. 174.3-174.6°.[21]

Reaction of 64 g. (0.5 mole) of 2,6-dimethyltetrahydro-1,4-pyrone with 1.0 mole of methylmagnesium iodide in diethyl ether resulted in a 55% yield of 2,4,6-trimethyltetrahydropyran-4-ol, b. p. 84-89° (18 mm.); the reported b. p. is 86-88° (18 mm.).[8] This material was separated into two distinct components by fractional distillation: the one had b. p. 85.0-85.6° (18 mm.), n^{20}_D 1.4500, d^{20}_4 0.9625, m. p. 41° (hygroscopic rhombohedrons from isopentane); the other had b. p. 88-89° (18 mm.), n^{20}_D 1.4532, d^{20}_4 0.9687, m. p. 51° (fine needles from isopentane). These two components were shown by mixing melting points to be identical with the corresponding substances obtained by hydration of the pyran mixture.

Dehydration of 25.6 g. (0.18 mole) of 2,4,6-trimethyl-

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[15] Paul, *Compt. rend.*, **211**, 645 (1940); see also Manchen and Schmidt (to General Aniline & Dye Corporation), U. S. Patent 2,314,454 (March 23, 1943).

[16] Clarke, *Am. Chem. J.*, **39**, 94 (1908); *Ber.*, **40**, 354 (1907), reports b. p. 168° (762 mm.) for 4-methylheptan-2-ol; this structure for VIII was confirmed by conversion of VIII to IX and X.

[17] "Selected Values of Properties of Hydrocarbons," API Research Project 44, Table 3a (June 30, 1945, and Dec. 31, 1948) gives b. p. 117.709° (760 mm.) and n^{20}_D 1.39792 for 4-methylheptane. A comparison of the infrared absorption spectrum of X with the spectra of all of the octanes positively identified the hydrocarbon as 4-methylheptane.

[18] Borsche and Thiele, ref. 8, report a boiling point of 95-100° (16 mm.) for the acetate of 2,4,6-trimethyltetrahydropyran-4-ol. This disagreement is not considered significant in view of the fact that these investigators reacted but 4 g. of alcohol with acetic anhydride and thus probably obtained insufficient product for accurate boiling point determination.

[19] Collie, *J. Chem. Soc.*, 617 (1891).

[20] Borsche, *Ber.*, **48**, 682 (1915).

[21] de Vrieze, ref. 9, reports b. p. 54-55° (11.5 mm.), d^{16}_4 0.9819, n^{16}_D 1.4424, and 2,4-dinitrophenylhydrazone, m. p. 177-178° for *cis*-2,6-dimethyltetrahydro-1,4-pyrone.

tetrahydropyran-4-ol, b. p. 84–89° (18 mm.) gave 20 g. (88% yield) of product of b. p. 129.0–136.6° (763 mm.), approximately 90%, of which, on redistillation, boiled at 133.0–136.2° (763 mm.) and had n^{20}_D 1.4410 and d^{20}_4 0.8622.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.86; H, 11.20.

The infrared absorption spectrum of this material was almost exactly identical with that of the pyran mixture obtained on dehydration of 2-methyl-2,4-pentanediol and showed the presence of both of the isomeric pyrans in approximately the same relative proportions as in material from the latter source.

Summary

Among the by-products of the dehydration of 2-methyl-2,4-pentanediol have been found acetaldehyde, isobutylene and a mixture of pyrans consisting of 3,6-dihydro-2,4,6-trimethyl-2H-pyran along with a minor amount of 2,6-dimethyl-4-methylenetetrahydropyran.

EMERYVILLE 8, CALIFORNIA RECEIVED MAY 8, 1950

[A CONTRIBUTION FROM THE LABORATORIES OF THE SHELL DEVELOPMENT COMPANY]

A Synthesis of Substituted Pyrans

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In the preceding paper[1] it was reported that the dehydration of 2-methyl-2,4-pentanediol gives as one of its products 3,6-dihydro-2,4,6-trimethyl-2H-pyran (I) along with a minor amount of a substance believed to be 2,6-dimethyl-4-methylenetetrahydropyran (II). Further investigation has indicated a mechanism for the formation of these compounds and has shown that the reactions involved can be generalized for the production of a variety of pyrans.[2]

Mechanism of Formation of the Pyrans.—The dehydration of 2-methyl-2,4-pentanediol gives under the conditions employed in the work described in the preceding paper largely 2-methyl- and 4-methyl-1,3-pentadienes along with 4-methyl-4-penten-2-ol, acetaldehyde, isobutylene and the aforementioned pyrans. Inasmuch as the pyrans contain eight carbon atoms, it was suspected that they are formed by reaction of acetaldehyde with either the diol, the methylpentadienes, or 4-methyl-4-penten-2-ol, and a number of experiments were performed in order to ascertain which of these combinations was their most likely source.

Acetaldehyde and 2-methyl-2,4-pentanediol were found to combine readily at about room temperature in the presence of acidic catalysts to give high yields of the cyclic acetal, 2,4,4,6-tetramethyl-*m*-dioxane. This compound decomposes slowly when heated at its boiling point with a trace of hydriodic acid and more rapidly with several volumes of very dilute hydrochloric acid[3] with formation of methylpentadiene, acetaldehyde and water.

Acetaldehyde and methylpentadiene, along with a trace of hydriodic acid, did not combine at room temperature, but interaction did occur slowly when the mixture was heated at 130–135° (under pressure) for five hours. From this reaction was obtained a fraction, representing a 10–15% conversion of the reactants, which appeared from its elemental composition, properties and infrared spectrum to be an impure mixture of the two pyrans and/or their isomers; a small amount of very high boiling condensation product was also obtained. Acetaldehyde and the diene at 185° (under pressure) in the absence of an acid catalyst formed only very high boiling condensation products.

The interaction of acetaldehyde and 4-methyl-4-penten-2-ol on the other hand took place very readily at below room temperature in the presence of acid with formation of 3,6-dihydro-2,4,6-trimethyl-2H-pyran (I) and 2,6-dimethyl-4-methylenetetrahydropyran (II), as well as 2,4,6-trimethyltetrahydropyran-4-ol (III)[4] and a substance of composition $C_{14}H_{26}O_2$ which may be the 4-methyl-4-penten-2-yl ether of III or possibly of 4-methyl-3-heptene-2,6-diol (see footnote 9); formation of higher condensates was negligible.

It thus appears that formation of the pyrans I and II during the dehydration of 2-methyl-2,4-pentanediol takes place by the interaction of acetaldehyde and either methylpentadiene or 4-methyl-4-penten-2-ol or both. However, in view of the ease with which the alcohol reacts, it is believed that this substance is the chief source of the pyrans formed during the diol dehydration.

Both the dehydration of the diol and the condensation between acetaldehyde and 4-methyl-4-penten-2-ol were found to be promoted by a variety of acid-acting substances. Suitable catalysts for the condensation were sulfuric and hydrochloric acids and anhydrous ferric chloride, all resulting in formation of the two pyrans (I and II) and 2,4,6-trimethyltetrahydropyran-4-ol (III); the use of anhydrous calcium chloride, however, yielded only the acetal of 4-methyl-4-penten-2-ol.

The initial step in the reaction between acetaldehyde and the unsaturated alcohol could be postulated to occur either at the olefinic linkage or at the hydroxyl group of the alcohol. In considering the first of these alternatives, the literature on the extensive studies of the reaction of aldehydes, particularly formaldehyde (and its polymeric forms),

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(1) Ballard, Holm, and Williams THIS JOURNAL, 72, 5734 (1950).

(2) Williams and Ballard (to Shell Development Co.), U. S. Patents 2,422,648 (June 17, 1947) and 2,452,977 (Nov. 2, 1948).

(3) Mikeska and Arundale (to Jasco, Inc.), U. S. Patent 2,350,517 (June 6, 1944).

(4) The steps leading to this product are apparently very stereoselective since but one of the three theoretically possible geometrical isomers was isolated from the reaction mixture.